# Aerogel Projects Ongoing in MSFC's Engineering Directorate

David A. Shular
MSFC/NASA
Mailstop: ED25
Huntsville, AL 35812
(256) 544-8734 (ph)
(256) 544-0800 (f)
email: David.A.Shular@msfc.nasa.gov

Gweneth A. Smithers
MSFC/NASA
Mailstop: ED34
(256) 544-0282 (ph)
(256) 544-7255
email: Gweneth.Smithers@msfc.nasa.gov

Joel L. Plawsky
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

## Introduction

When we speak of an aerogel material, we are referring more to process and structure than to a specific substance. Aerogel, considered the lightest solid material, has been made from silica for seventy years. Resorcinol-formaldehyde, organic aerogels have been developed more recently. However, aerogel can be made from almost any type of substance, even lead. Because an aerogel is mostly air (about 99 %), the solid substance used will affect the weight very little.

The term "aerogel" connotes the sol-gel process used to manufacture the material. The aerogel begins as a liquid "sol," becomes a solid "alcogel," and is then dried to become an "aerogel." The final product has a unique structure, useful for exploitation. It is an "open pore" system with nano-sized particles and pores, has very high surface area, and is highly interconnected. Besides low weight, aerogels have ultimate (lowest) values in other properties: thermal conductivity, refractive index, sound speed, and dielectric constant. Aerogels were first prepared in 1931 by Steven Kistler, who used a supercritical drying step to replace the liquid in a gel with air, preserving the structure (1). Kistler's procedure involved a water-to-alcohol exchange step; in the 1970's, this step was eliminated when a French investigator introduced the use of tetramethylorthosilicate. Still, alcohol drying involved dangerously high temperatures and pressures. In the 1980's, the Microstructured Materials Group at Berkeley Laboratory found that the alcohol in the gel could be replaced with liquid carbon dioxide before supercritical drying, which greatly improved safety (2). The most recent major contribution has been that of Deshpande, Smith and Brinker in New Mexico, who are working to eliminate the supercritical drying step (3). When aerogels were first being developed, they were evaporatively dried. However, the wet gel, when dried, underwent severe shrinkage and cracking; this product was termed "xerogel." When the autoclave drying step was introduced, the final product was without

cracks and showed only minimal shrinkage; this product was termed "aerogel." In the 1990's, Deshpande, Smith and Brinker developed an evaporative drying procedure in which the wet gel is chemically "capped" so that the material, which undergoes shrinkage, springs back to its original size when evaporatively dried. This new type of xerogel, while uncracked and almost the same size as the wet gel, differs from the autoclave-dried product in that it is less porous (approximately 70%, as compared to 99% for aerogels).

The unique structure of an aerogel has suggested many diverse applications. In addition to the focus on superinsulation, aerogel has been considered or used in the following applications: catalyst support, micrometeroid capture, subatomic particle detection, impaction safety, desalination, toxicity sensing, acoustic and electrical insulation, and optical coatings (4, 5). Nanocomposite work is an active area in aerogel research. Aerogels are nanomaterials because of their nano-sized pores and particles. When aerogels are used in composite manufacture, the aerogel is the substrate, to which another phase (nano or larger) is added. The second phase can be added during the sol-gel processing (before drying), through the vapor phase (after drying), or the aerogel backbone can be chemically modified through reactive gas treatment.

The problem with aerogels is their low tensile strength and lack of elasticity. Therefore, the challenge is to find ways to make them stronger or ways to circumvent the strength issue. Organic aerogels have slightly higher strength than base silica aerogels, while the carbonized version has 3-5 times the break strength of the base aerogel.

A standard silica aerogel has a thermal conductivity of about 17 mW/M-°K (0.00980075 BTU-ft/hr-ft$^2$-F). This is an order of magnitude lower than the cryogenic foams that NASA currently uses today. A carbonized silica has about 13 mW/M-°K (0.0075 BTU-ft/hr-ft$^2$-F). These values are at atmospheric pressure. At pressures of around 50 torr, these values drop (and flatten out) to 8 and 4 mW/M-$^o$K (0.0046 and 0.0023 BTU-ft/hr-ft$^2$-F) respectively.

The passage of thermal energy occurs in three modes, solid conductivity, gaseous conductivity, and radiative transmission. Solid conduction is limited due to the fact that the aerogels possess such a small amount of solid material. These solids consist of very small particles linked together in a three-dimensional network with many "dead-ends." This makes any thermal conduction extremely ineffective. Gaseous conduction is limited by the fact that the gas must follow a tortuous path, and with pore sizes less than the mean free path of air, the gaseous molecules are more likely to impact the pore surface before they collide with another gas molecule. The third method of transport, radiative transmission, is the primary mode of heat transfer in aerogels. Basic silica aerogels are reasonably transparent in the infrared region, especially between 3-5 microns. At low temperatures the radiative component is not a significant problem. At higher temperatures, carbon can be added as an effective absorber of infrared radiation.

There is work going on at NASA's Ames Research Center, and other places, to address radiative heat transfer. One method involves infusion or encapsulation of the aerogel into another material. Ames has developed an aerogel infused AETB (Alumina Enhanced Thermal Barrier)

tile, like what is currently flown on Shuttle, in hope of producing a single material that performs both cryo and aero-heating insulation duties in a single material.

In the Engineering Directorate at MSFC, our approach to the research and development of aerogel materials recognizes our relative inexperience in this technology area. We have chosen to partner with other NASA Centers, universities and industry to make the most of our mutual efforts in aerogel research.

**Composite, Cryogenic, Conformal, Common Bulkhead, Aerogel-insulated Tank**

Through award of a NASA Research Announcement (NRA), a Composite, Cryogenic, Conformal, Common Bulkhead, Aerogel-insulated Tank (CBAT) is being developed at MSFC. The CBAT team includes engineers from the Structures, Mechanics & Thermal Department (S,M & T) and the Materials, Processes & Manufacturing Department (MPM). Thiokol and Sverdrup also provide engineering support. This work is funded as a next generation RLV project. The intended propellants are liquid oxygen (LOX) and high-grade kerosene (RP); however, liquid nitrogen and water will be used to test this subscale tank. The tank will contain enough propellant to fire the Fastrac engine for 15 seconds. Tank pressure and compressive loads will also be based on the Fastrac engine. Aerogel insulation is being used at two locations: in the common bulkhead area (between the LOX and RP tanks) and around the skirt that surrounds the two tanks.

We explored a number of aerogel possibilities for the common bulkhead area. At the current time, Nanogel $^{TM}$ (an evaporatively dried, silica-based xerogel which has been powdered and compressed, with additives, into a near monolith) is our baseline component. For testing, we obtained 8-inch diameter, _ inch thick disk samples of Nanogel $^{TM}$ from Nanopore, Inc. in Albuquerque. The ASTM procedure for thermal conductivity testing requires samples of this size and shape. Because of the loads which will be experienced by the xerogel when the tank is pressurized, we asked Nanopore to compact this material at 75 psi, instead of 15 psi which is standard practice. Nanopore normally seals the material under a slight vacuum with a metallized, plastic laminate wrapper. We requested three types of samples: vacuum-sealed with air; sealed without vacuum; and krypton filled, sealed without vacuum. We also obtained one sample (vacuum-sealed with air) which was compacted with the standard 15 psi. The 75 psi samples were tested for thermal conductivity and compression strength. The 15 psi sample was tested for compression strength only. The results of these tests are shown in Tables 1 through 3 and Figures 1 through 4. Since the vacuum-sealed sample should insulate better than the Krypton-filled sample, we believe the vacuum-sealed sample may have lost vacuum. Attempts to perform thermal conductivity testing at cryogenic temperatures were not successful. The Holometrix Micromet Model GHP-200 employed was designed for higher temperatures. We are currently making plans to perform cryogenic testing of these samples at another facility. Thermal conductivity testing was performed by Scott Taylor of ASRI; he used ASTM Method C-177, Standard Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded-Hot-Plate Apparatus. Compressive fatigue testing was performed by Andrew Hodge, MPM Department.

In cooperation with Dr. Susan White at NASA's Ames Research Center, we are also pursuing an alternative type of aerogel for the common bulkhead area. Nomex™ honeycomb was cut into 8-inch disks here at MSFC, and subsequently shipped to Ames. In Dr. White's laboratory, an organic aerogel, formulated for compatibility with the honeycomb material will be used to fill the honeycombs, which will then be supercritically dried in an autoclave. These samples will be shipped back to MSFC for testing.

Around the skirt, we plan to install an aerogel blanket system. Because of his experience with aerogel blankets, we asked Mr. James Fesmire of Kennedy Space Center to assist us in this effort. The insulation system will include a Teflon-coated fiberglass cloth (beta cloth) on the cold side, an aerogel composite blanket (from Aspen Systems in Boston), and Silverlux™ film on the warm side. We are currently devising a mechanism by which CBAT team members at MSFC and Cryogenic Testbed personnel at KSC can exchange services in a way that is beneficial to both Centers.

**Xerogel Optical Toxicity Sensor**

Because of his expertise in aerogel materials, Dr. Joel Plawsky, a professor at Rensselaer Polytechnic Institute, was invited to spend the summers of 1999 and 2000 as a Faculty Fellow in the MPM Department at MSFC. Our awareness of the environmental and safety issues associated with the standard autoclave procedure used in production of aerogel and our study of recent advances in elimination of the autoclaved, supercritical drying step, led us to pursue, with Dr. Plawsky, aerogel production which employed evaporative drying rather than autolcave drying. This work, performed in 1999, laid the foundation for work performed in 2000 to develop an optical toxicity sensor.

Our goal during the summer of 1999 was to determine if the evaporative drying step used for thin-film aerogels in Dr. Plawsky's lab at RPI could be adapted to produce thicker, monolithic aerogels. Tetraethoxysilane (TEOS), ethanol, water, and hydrochloric acid were mixed and heated for 90 minutes. Acid catalysis promoted hydrolysis of the TEOS and initial polymerization. The precursor sol was then mixed with a solution of ammonium hydroxide. At room temperature, base catalysis promoted branching and crosslinking of the sol leading to gel formation in about 40 minutes. The wet gel was aged in a two-step process, performed at room temperature. In the first step, the gel was placed in a solution of ammonium hydroxide and ethanol, where it remained on a shaker table for 24 hours. The gel was then rinsed in ethanol and immersed in a solution of TEOS and ethanol. The gel was then aged from 24 to 72 hours at room temperature. Following this step, the gel was thoroughly rinsed in ethanol. Afterwards, the gel was immersed in hexamethyldisiloxane (HMDSO), and the capping agent was slowly added to yield a 10 mole% solution of trimethylchlorosilane in HMDSO. Gels were allowed to sit in the capping solution for 24 –48 hours on the shaker table. Subsequently they were flipped and immersed in a new solution to ensure complete treatment. After capping, the gels were washed in HMDSO again before drying began. Initial experiments drying the gels at room temperature failed. Eventually, the procedure was modified and resulted in successfully dried gels. The gel was placed in a closed petri dish (2" in diameter) which was drilled with a 1/16" hole at the top. The gels were placed on x-shaped teflon supports to elevate them from the bottom surface of the dish and remove any capillary suction there. This allowed the gels to

expand and contract freely during drying. The petri dishes were set on a hot plate, on top of a crucible insulator, and covered with a 600 ml fritted glass filter. The filter controlled the evaporation rate and kept the draft from the hood away from the specimen. Depending on the sample, drying took from 3 to 24 hours. Samples produced were 1/8" thick.

Aerogels exhibit high surface area, stability, and transparency. They can easily transport gases and can be filled with other phases. These properties make aerogels well-suited for use in optical sensors. When Dr. Plawsky returned to MSFC in the summer of 2000, we began work on a toxicity sensor which might have application in a closed-system situation like Space Station, where toxic chemicals must be monitored at a highly sensitive level. Figure 5 illustrates the plan for this sensor. Our plan for the summer was to continue development of various types of aerogel using the manufacturing procedure developed during the previous summer. These aerogels would be candidates for the layer that covers the waveguide. The waveguide element of this device is being developed at RPI by Dr. Plawsky and his graduate students. The aerogel or xerogel material forms the cladding of an integrated optical waveguide. The core material can be made of anything that has a higher refractive index than the xerogel and that the xerogel will adhere to. The xerogel component acts as the sensing element of the device since it can contain organic functionality that will interact with materials in the atmosphere. These are absorbed into the xerogel, changing its optical properties. The changes are read by the waveguide either as a change in the propagation characteristics of the waveguide or as a change in the intensity of the light as it passes through the waveguide. The sensitivity of the device comes from the great surface area of the xerogel and the large optical interaction length of the waveguide. At this writing, we are completing manufacture of these types of xerogels at MSFC. Two are hybrid silica-titania and silica-zirconia gels. These materials can be used as oxidation substrates for destruction of volatile organic compounds (6) in spacecraft. The high surface area of xerogels makes them well-suited for making compact chemical reactor systems (7). We are also making organic/inorganic hybrid xerogels with amino, mercapto, cyano, and saturated hydrocarbon functionality. Amino functional groups can be used to absorb and sense acid vapors, mercapto groups are useful for incorporating metals into the gels and using the metals as sensing elements, cyano groups are reactive functional groups to acidic and basic groups and the hydrocarbon groups are meant for absorption of nonpolar organic constituents. In addition, the amino and cyano groups can also be used to immobilize enzymes or antibodies into the gels for biological operations (8). In all cases the interaction of the compound of interest with the functional groups in the xerogel changes the optical properties of the xerogel and provides for the sensing function when the xerogel is used as a cladding for the optical waveguide.

**Thermally Integrated Structures**

Thermally Integrated Structures (ThIS) are a long-term goal at MSFC. NASA needs a reusable launch vehicle (RLV), single-stage-to-orbit, which utilizes liquid oxygen/liquid hydrogen chemical propulsion. To attain this goal, vehicle mass fraction must be high, 0.9 or greater. Vacuum specific impulse must be maximized, but realistically will be limited to ~ 460 seconds. The vehicle should look and operate as an aircraft. Vehicle volume must be reasonable to enable handling and operability.

A major difference between aircraft and RLV's is the "use temperature" of major structures. RLV aerodynamic surfaces can be exposed to environments resulting in surface temperatures up to 1800$^{o}$F (leading edges, up to 3000$^{o}$F). These hot surfaces must be non-catalytic. Cryogenic tankage will be exposed to –420$^{o}$F, and must be compatible with liquid and gaseous oxygen and hydrogen. Heat leakage through the structure must be small. No cryopumping within the structure can be tolerated; the structure must be impermeable. The system must be durable, easily weatherproofed, lightweight, manufacturable and maintainable. It must have low operational costs. Material systems must be manufacturable in large sections. Joining and attachment techniques must be easily implemented.

Like aircraft, our current design approach includes use of lightweight materials of construction. Unlike aircraft, we add a Thermal Protection System (TPS) and cryogenic insulators to enable use temperatures for these structures. These additions add weight and cost, while reducing operability. These systems also add complexity in the area of attachments and add requirements such as allowable bond-line temperatures, complicating the design problem.

Estimates of RLV GLOW have indicated that this design approach, with these materials of construction and LOX/LH2 propulsion, does not meet SSTO feasibility requirements (mass fraction at an operable vehicle volume). Graphite-epoxy dry structures and integral cryotankage were thought to offer weight efficiency sufficient to enable SSTO, but if current RLV estimates derived from X-33 experience do not enable SSTO, then alternate approaches must be considered. One promising technology for RLV is advanced and integrated fundamental materials of construction for airframe and cryotank structures. We want to investigate feasibility of development of lightweight Thermally Integrated Structures with a large range of operating temperatures, and low heat transfer through the thickness of the material system.

The weight of such a material system must be significantly less than standard designs (which use lightweight materials with lightweight cryogenic insulators and TPS materials. For an investigation like this, we are considering a titanium honeycomb (use temperature ~ 1200F) filled with a high temperature aerogel. Very low heat transfer from face to face would be the goal of such as system, with all materials capable of withstanding both cryogenic to aero entry use temperature, as well as temperature gradients across the structure. Life should be at least 100 thermal/structural cycles. Manufacturability in very large sections is a key to operability. A severe limitation in the areas of cost and operability for current TPS material systems is the need to attach thousands of piece parts to very large structures.

The Thermodynamics and Heat Transfer Group in the Structures, Mechanics &Thermal Department (SMT) at MSFC have prepared a computational model which employs a titanium honeycomb core utilizing solid fill carbon aerogel. The facesheets are aluminum on the inside surface and titanium on the outer surface. The core dimensions consist of 3/8" diameter centers with a wall thickness of 0.005". The baseline design is for a 1" thick panel with counterbores of 2" diameter and 3/8" deep. The counterbores are oriented such that there is a slight overlap in order to provide a design in which there is no direct conduction path through the thickness of the panel. In the actual panel to be constructed, the counterbores will probably be square such that the edges can be aligned in order to ensure that there are no gaps created by the overlying circles which might allow for a more direct conduction path. Several densities of carbon aerogel have

been considered in an attempt to learn which density may be the best choice. According to the literature from the national labs, radiation is the primary mechanism of energy transport at elevated temperatures for generic aerogels; the solid conductivity is small in comparison. However, since this design is a closed system with direct contact among all materials (and the added carbon is an infrared absorber) conduction has been the primary focus. Property data is still being collected. The SMT and the MPM Departments are writing proposals and actively seeking funding for Thermally Integrated Structures projects.

**Table 1. Apparent Thermal Conductivity of Nanogel™ TI-6000, 800 mbar abs. No Vacuum**

| *Sample Position* | *Thickness (mm)* | *Diameter (mm)* | *Mass (g)* | *Density (kg/m$^3$)* |
|---|---|---|---|---|
| Top | 13.20 | 203.20 | 96.20 | 224.73 |
| Bottom | 13.80 | 203.20 | 94.10 | 210.27 |

| *Mean Temperature, Degrees C (Deg F)* | *Apparent Thermal Conductivity, W/mK* |
|---|---|
| 4.2 (39.6) | 0.016466 |
| 4.2 (39.6) | 0.016826 |
| 9.4 (49.0) | 0.017191 |
| 9.4 (48.9) | 0.017326 |
| 18.4 (65.1) | 0.018205 |
| 18.4 (65.2) | 0.018246 |
| 35.1 (95.1) | 0.019066 |
| 35.0 (95.0) | 0.018990 |
| 56.4 (133.5) | 0.020265 |
| 60.2 (140.3) | 0.020675 |

**Table 2. Apparent Thermal Conductivity of Nanogel™ TI-6000, 1 mbar abs. Vacuum**

| *Sample Position* | *Thickness (mm)* | *Diameter (mm)* | *Mass (g)* | *Density (kg/m$^3$)* |
|---|---|---|---|---|
| Top | 12.50 | 203.20 | 97.80 | 241.26 |
| Bottom | 12.40 | 203.20 | 94.50 | 235.00 |

| *Mean Temperature, Degrees C (Deg F)* | *Apparent Thermal Conductivity, W/mK* |
|---|---|
| -5 (23) | 0.011513 |
| 2.2 (36) | 0.011339 |
| 13.8 (57) | 0.012672 |
| 18.3 (65) | 0.012885 |
| 32.8 (91) | 0.013585 |
| 47.7 (118) | 0.012485 |

**Table 3. Apparent Thermal Conductivity of Nanogel™ TI-6000, 800 mbar abs. Krypton**

| *Sample Position* | *Thickness (mm)* | *Diameter (mm)* | *Mass (g)* | *Density (kg/m$^3$)* |
|---|---|---|---|---|
| Top | 12.80 | 203.20 | 96.90 | 233.44 |
| Bottom | 13.70 | 203.20 | 99.40 | 223.73 |

| *Mean Temperature, Degrees C (Deg F)* | *Apparent Thermal Conductivity, W/mK* |
|---|---|
| 1.1 (34) | 0.010216 |
| 6.1 (43) | 0.010266 |
| 21.7 (71) | 0.011066 |
| 32.8 (91) | 0.012039 |

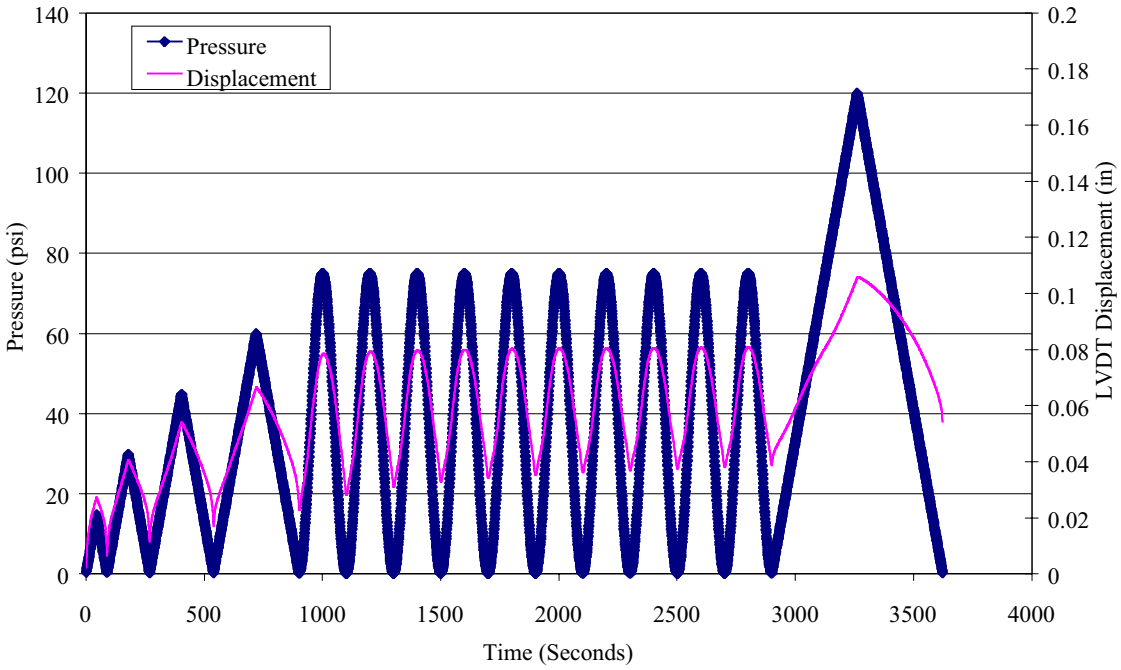


**Figure 1. Compressive Fatigue Test of Xerogel Disk (75 psi, No Vacuum)**

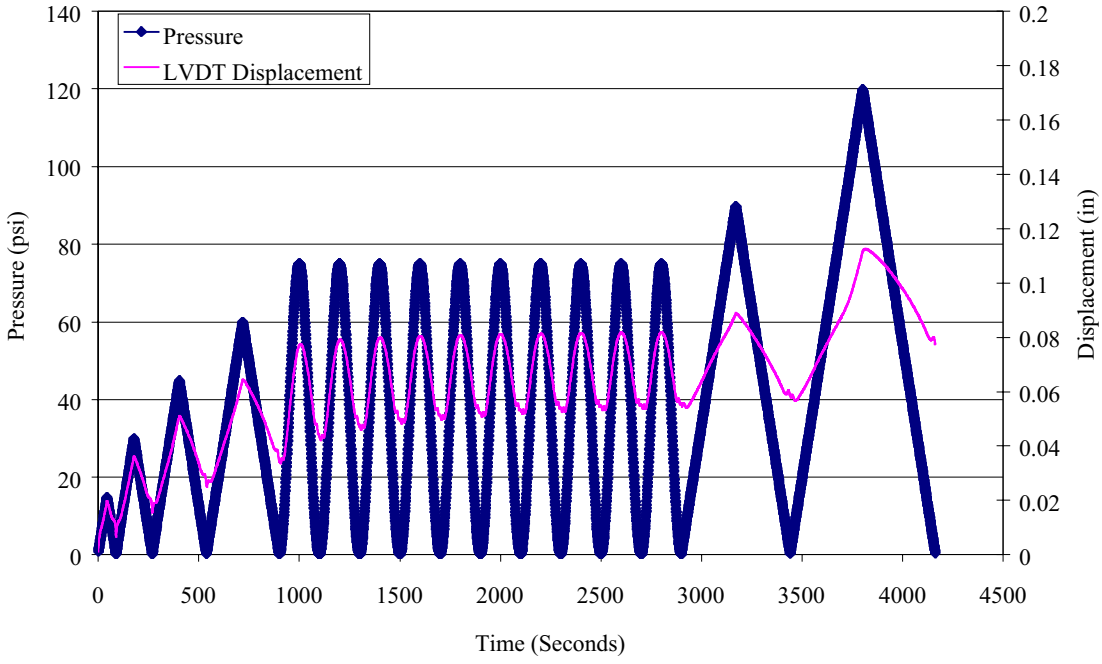


**Figure 2. Compressive Fatigue Test of Xerogel Disk (75 psi, Vacuum)**

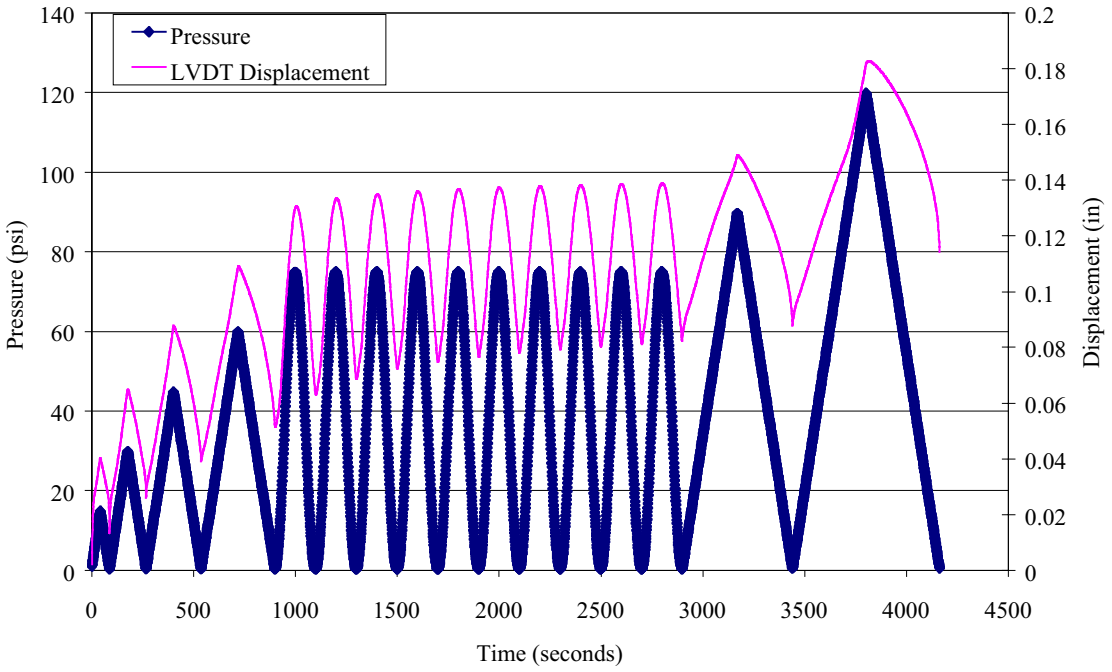


**Figure 3. Compresive Fatigue Test of Xerogel Disk (75 psi, Krypton Filled)**

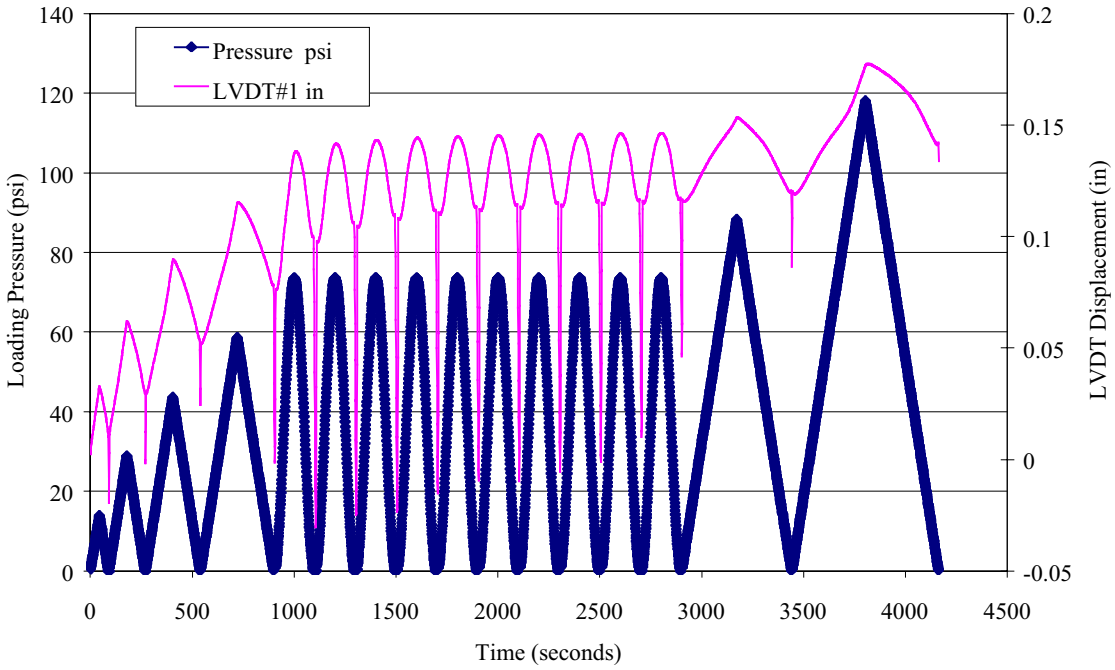


**Figure 4. Compressive Fatigue Test of Xerogel Disk (15 psi, Vacuum)**

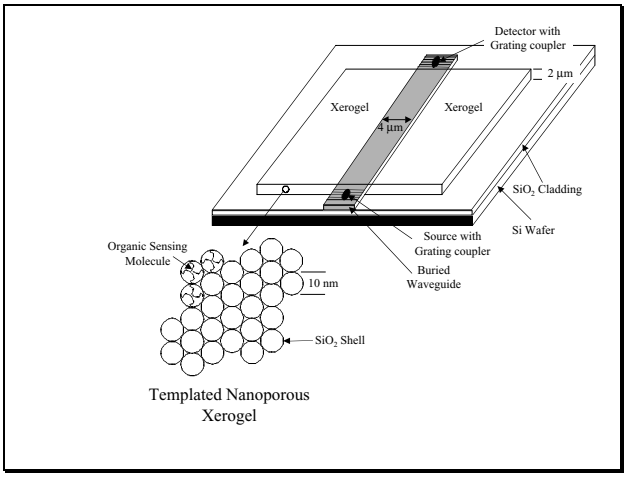


**Figure 5. Xerogel Sensor Concept**

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